A vibrational spectroscopic study of the phosphate mineral cyrilovite
$\text{Na(Fe}^{3+}\text{)}_3(\text{PO}_4)_2(\text{OH})_4\cdot2(\text{H}_2\text{O})$ and in comparison with wardite

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ABSTRACT

Vibrational spectroscopy enables subtle details of the molecular structure of cyrilovite to be determined. Single crystals of a pure phase from a Brazilian pegmatite were used. Cyrilovite is the Fe$^{3+}$ member of the wardite group. The infrared and Raman spectroscopy were applied to compare the structure of cyrilovite with that of wardite. The Raman spectrum of cyrilovite in the 800 to 1400 cm$^{-1}$ spectral range shows two intense bands at 992 and 1055 cm$^{-1}$ assigned to the \( \nu_1 \text{PO}_4^{3-} \) symmetric stretching vibrations. A series of low intensity bands at 1105, 1136, 1177 and 1184 cm$^{-1}$ are assigned to the \( \nu_3 \text{PO}_4^{3-} \) antisymmetric stretching modes. The infrared spectrum of cyrilovite in the 500 to 1300 cm$^{-1}$ shows much greater complexity than the Raman spectrum. Strong infrared bands are found at 970 and 1007 cm$^{-1}$ and are attributed to the \( \nu_1 \text{PO}_4^{3-} \) symmetric stretching mode. Raman bands are observed at 612 and 631 cm$^{-1}$ and are assigned to the \( \nu_4 \) out of plane bending modes of the \( \text{PO}_4^{3-} \) unit. In the 2600 to 3800 cm$^{-1}$ spectral range, intense Raman bands for cyrilovite are found at 3328 and 3452 cm$^{-1}$ with a broad shoulder at 3194 cm$^{-1}$ and are assigned to OH stretching vibrations. Sharp infrared bands are observed at 3485 and 3538 cm$^{-1}$. Raman spectroscopy complimented with infrared spectroscopy has enabled the structure of cyrilovite to be ascertained and compared with that of wardite.

Keywords: cyrilovite, wardite, phosphate, hydroxyl, Raman spectroscopy, infrared
Introduction

Cyrilovite [1] is a hydrated hydroxyl sodium ferric phosphate \( \text{Na(Fe}^{3+}\text{)}_3(\text{PO}_4)_2(\text{OH})_4\cdot 2(\text{H}_2\text{O}) \) [2, 3]. The mineral belongs to the wardite group [4], which also includes millisite. The crystal structures of cyrilovite have been solved [2, 5] and was further refined by Cooper et al. [6]. The cell dimensions are \textit{Space Group: \( P4_12_12 \) or \( P4_32_12 \).} \( a = 7.03(1), c = 19.04(1), Z = 4. \) The structures contain layers of two kinds of corner-linked –OH bridged MO\(_6\) octahedra (M \( = \) Al, Fe), stacked along the tetragonal \( C \)-axis in a four-layer sequence and linked by PO\(_4\) groups. Within a layer, e.g. around the (001) plane, two independent pairs of symmetry-correlated –OH groups are arranged in the equatorial pseudo-planes of one kind of MO\(_6\) octahedra [2, 5]. The mineral is yellow, orange, to brown with vitreous lustre.

Cyrilovite is known from many localities. The mineral was first described from Cyrilov Pegmatite, Moravia, Czech Republic [1]. In Australia it was found in Campbells Creek [7], in Northparkes, New South Wales [8] and in Wiperaminga Hill West Quarry [9]. Other significant occurrences were described in Brazil [10], Germany [11] and Italy [12, 13] among others [14].

To the best knowledgement of the authors, vibrational spectroscopy studies of cyrilovite are rare in the literature [15, 16]. Tarte et al. [16] collected the infrared spectra of five samples of cyrilovite \( \text{NaFe}_3(\text{PO}_4)_2(\text{OH})_4\cdot 2(\text{H}_2\text{O}) \) and wardite. Cyrilovite is analogous to wardite, with ferric iron replacing the aluminium in the structure. It is likely that solid solutions of the two minerals are formed with varying amounts of ferric ion and aluminium in the structure.

The mineral wardite is capable of crystallizing in a similar form to that of cyrilovite because of their closely related chemical compositions. Between wardite’s composition, \( \text{NaAl}_3(\text{PO}_4)_2(\text{OH})_4\cdot 2(\text{H}_2\text{O}) \), and cyrilovite’s composition, \( \text{NaFe}_3(\text{PO}_4)_2(\text{OH})_4\cdot 2(\text{H}_2\text{O}) \), these minerals are able to form end members of a series of solid solutions. Either of the two minerals can occur in various proportions in a series of solid solutions in the wardite mineral group. Cyrilovite is a rare accessory mineral in some oxidizing phosphate-bearing granite pegmatites and iron deposits. The vibrational spectrum is dependent upon the ratio of the Al/Fe. Tarte et al. [16] found that the two minerals wardite and cyrilovite can be distinguished by the spectral patterns of the OH stretching region in the infrared spectrum [16]. These workers did not interpret the spectra of the phosphate because of complexity and
no detailed assignment was given. Breitinger et al. [15] reported the combined vibrational spectra of a natural wardite. The same authors used a full array of techniques including inelastic neutron scattering, infrared, Raman and near infrared techniques. These workers used a natural wardite with significant amounts of ferric iron in the structure. In other words the sample analysed was fundamentally a solid solution of wardite and cyrilovite, but at the wardite end. The original papers on the infrared spectra of isolated phosphate units were published by Lazarev [17]. Phosphates structures may vary between different minerals. Usually they have rather low symmetry: orthorhombic, monoclinic, or even triclinic [18]. Farmer based upon the work of Petrov et al. [19-21] made a comparison of the results of the vibrational spectrum of a series of phosphates.

Raman spectroscopy has proven very useful for the study of minerals [22-25]. Indeed, Raman spectroscopy has proven most useful for the study of diagenetically related minerals where isomorphic substitution may occur as with wardite and cyrilovite, as often occurs with minerals containing phosphate groups. This paper is a part of systematic studies of vibrational spectra of minerals of secondary origin in the pegmatite rocks. The objective of this research is to report the Raman and infrared spectra of cyrilovite and to relate the spectra to the molecular structure of the mineral.

**Experimental**

*Samples description and preparation*

The cyrilovite sample studied in this work was collected from the Sapucaia mine (also named as Proberil mine), a lithium-bearing pegmatite located in the Conselheiro Pena Pegmatite district (CPD), one of the eleven metallogenetic subdivisions of the Eastern Brazilian Pegmatite Province (EBP) in Minas Gerais [25]. The Sapucaia mine is an important source for rare and unusual phosphate minerals and is the type locality for a number of rare phosphates such as moraesite, barbosalite, frondelite and ruifrancoite.

Cyrilovite occurs in Sapucaia mine as yellow to orange aggregates of crystals up to 0.05 mm in size, in association with frondelite, zanazziite, cacoxenite and variscite. The sample was incorporated to the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAA-175. The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. The cyrilovite
sample was phase analyzed by X-ray diffraction. Scanning electron microscopy (SEM) in the EDS mode was applied to support the mineral characterization.

**Raman spectroscopy**

Crystals of cyrilovite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarised light at 633 nm and collected at a nominal resolution of 2 cm\(^{-1}\) and a precision of ± 1 cm\(^{-1}\) in the range between 100 and 4000 cm\(^{-1}\). Some of these mineral fluoresced badly at 633 nm; as a consequence other laser excitation wavelengths were used especially the 785 nm laser. Repeated acquisitions on the crystals using the highest magnification (50x) were accumulated to improve the signal to noise ratio of the spectra. Spectra were calibrated using the 520.5 cm\(^{-1}\) line of a silicon wafer. Previous studies by the authors provide more details of the experimental technique. Alignment of all crystals in a similar orientation has been attempted and achieved. However, differences in intensity may be observed due to minor differences in the crystal orientation.

**Infrared spectroscopy**

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–500 cm\(^{-1}\) range were obtained by the co-addition of 128 scans with a resolution of 4 cm\(^{-1}\) and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel ‘Peakfit’ software package that enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentzian-Gaussian cross-product function with the minimum number of component bands used for the fitting process. The
Lorentzian-Gaussian ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of $r^2$ greater than 0.995.

**Results and Discussion**

**Chemical characterization**

The SEM image of cyrilovite sample studied in this work is shown in Figure 1. Cyrilovite crystals show a tetragonal form and the crystal aggregate forms a rosette habitus. Qualitative chemical composition shows a homogeneous phase, composed by Na, Fe and P, with minor amounts of Al and Mn (Figure 2). The presence of Mn is indicative of the hypothetical existence of a manganese end member in a Fe-Mn series.

**Spectroscopy**

The Raman spectrum of cyrilovite in the 100 to 4000 cm$^{-1}$ spectral range is illustrated in Figure 3a. This spectrum shows the position of the Raman bands and their relative intensities. It is obvious that there are large parts of the spectrum where no intensity is observed. Therefore, the spectrum is subdivided into sections according to the type of vibration being investigated. In this way the precise position of the bands can be detailed. The infrared spectrum of cyrilovite in the 500 to 4000 cm$^{-1}$ spectral range is shown in Figure 3b. The reflectance spectrum starts at 500 cm$^{-1}$ because the ATR cell absorbs all infrared radiation below this wavenumber. As for the Raman spectrum, the infrared spectrum is subdivided into sections depending upon the type of vibration being examined. The complete infrared spectrum displays the position of the infrared bands and their relative intensity.

The Raman spectrum of cyrilovite in the 800 to 1400 cm$^{-1}$ spectral range is reported in Figure 4a. The Raman spectrum is dominated by two intense bands at 992 and 1055 cm$^{-1}$. These two bands are assigned to the $\nu_1$ PO$_4^{3-}$ symmetric stretching vibrations. Two intense bands are observed reflecting two non-equivalent phosphate units in the cyrilovite structure. A comparison may be made with the spectrum of wartdite. The Raman spectrum is dominated by two intense bands at around 995 and 1051 cm$^{-1}$. The spectra appear to differ considerably from that obtained by Breitinger et al. [15]. These researchers used FT-Raman to obtain their
spectrum and found overlapping Raman bands at 999 and 1033 cm\(^{-1}\) and assigned these bands to the \(\nu_1\) PO\(_4^{3-}\) symmetric stretching and \(\nu_3\) PO\(_4^{3-}\) antisymmetric stretching modes. The difference in the spectra between our Raman work and that of Breitinger et al. may be attributed to the improved technology of the Raman spectrometer with greater resolution. The Raman spectrum (Figure 4a) shows a resolved component band at 1013 cm\(^{-1}\). There is also a shoulder band at 974 cm\(^{-1}\). Breitinger et al. [15] also assigned the band at 999 cm\(^{-1}\) to AlOH deformation modes. In this work the band at 992 cm\(^{-1}\) is very sharp and well resolved and is assigned to a phosphate stretching vibration.

A series of low intensity bands are noted at 1105, 1136, 1177 and 1184 cm\(^{-1}\). These bands are assigned to the \(\nu_3\) PO\(_4^{3-}\) antisymmetric stretching modes. The Raman spectrum of wardite shows a group of low intensity bands are observed at 1084, 1108, 1120, 1140 and 1186 cm\(^{-1}\). Breitinger et al. [15] did not report any bands in these positions in the Raman spectrum of synthetic wardite. These researchers reported infrared bands at 1058 (strong) with shoulders at 1129 and 1168 cm\(^{-1}\) and assigned these bands to \(\delta\text{Al}_2\text{OH}\) deformation modes. A low intensity broad band at 884 cm\(^{-1}\) (a), 902 cm\(^{-1}\) (b) and 893 cm\(^{-1}\) (c) are assigned to a water librational mode. In the work of Breitinger et al. [15] a broad low intensity band was found at around 800 cm\(^{-1}\) and was attributed to water librational modes. In the Raman spectrum of cyrilovite two component bands are observed at 811 and 852 cm\(^{-1}\). These bands may be attributed to the water librational modes. Normally the intensity of water librational modes are of a quite low intensity in the Raman spectrum but may show significantly greater intensity in the infrared spectrum.

The infrared spectrum of cyrilovite in the 500 to 1300 cm\(^{-1}\) spectral range is shown in Figure 4b. The infrared spectrum of cyrilovite shows much greater complexity than the Raman spectrum. It is noted that the two infrared bands at 818 and 839 cm\(^{-1}\) attributed to the water librational modes show much greater intensity. Strong infrared bands are found at 970 and 1007 cm\(^{-1}\) and are attributed to the \(\nu_1\) PO\(_4^{3-}\) symmetric stretching mode. The observation of these two bands supports the concept that the phosphate units in the cyrilovite structure are not equivalent. A series of infrared bands at 1036, 1064, 1097 and 1154 cm\(^{-1}\) are assigned to the \(\nu_3\) PO\(_4^{3-}\) antisymmetric stretching modes. In the infrared spectrum of wardite, bands are observed at 1039, 1056, 1069, 1084, 1102, 1135 and 1165 cm\(^{-1}\). Some of these bands may also be due to the \(\delta\text{Al}_2\text{OH}\) deformation modes, in harmony with the assignment of Breitinger et al. He and his co-workers stated that the deceptively simple strong IR band centered at
1059 cm\(^{-1}\) contains at least four components of \(\nu(P0_4)\) generated by lifting of the originally threefold degeneracy of \(\nu_3(P0_4)\) and activation of \(\nu_1(P0_4)\) due to the general position of \(P0_4\) and again at least four components of the deformation modes \(\delta(\text{Al}_2\text{OH})\) involving the two pairs of the non-equivalent OH groups. In this work we have obtained much greater resolution and these components are resolved into the component bands.

The Raman spectrum of cyrilovite in the 300 to 800 cm\(^{-1}\) spectral range and in the 100 to 300 cm\(^{-1}\) spectral range are displayed in Figures 5a and 5b. Raman bands are observed at 612 and 631 cm\(^{-1}\) and are assigned to the \(\nu_4\) out of plane bending modes of the \(P0_4^{3-}\) and \(HPO_3^{2-}\) units. In the Raman spectrum of wardite, bands are observed at 605 and 618 cm\(^{-1}\) with shoulders at 578 and 589 cm\(^{-1}\). Breitinger et al. assigned these bands to \(\nu(\text{Al(O/OH)}_6)\) stretching vibrations. No phosphate bending modes in the work of Breitinger et al. were reported. The Raman spectrum of crystalline NaH\(_2\)PO\(_4\) shows Raman bands at 526, 546 and 618 cm\(^{-1}\). A series of Raman bands for cyrilovite at 411, 437, 482 and 498 cm\(^{-1}\) are observed. These bands are attributed to the \(\nu_2\) \(P0_4^{3-}\) and \(H_2P0_4\) bending modes. A comparison may again be made with the Raman spectrum of wardite. The series of Raman bands at 388, 400, 455, 478 and 502 cm\(^{-1}\) for wardite are attributed to the \(\nu_2\) \(P0_4^{3-}\) bending modes. Raman bands at 317, 446 and 515 cm\(^{-1}\) for wardite reported by Breitinger et al. [15] were assigned to vibrational modes of the \(\text{AlO}_6/\text{AlOH}_6\) units. However, this assignment differs from the assignments attributed in this work. Breitinger et al. [15] did not assign any of the Raman bands in their spectra to phosphate bending modes; yet the mineral is very rich in phosphate units and consequently the phosphate bending modes should be observed. An intense Raman band is observed at 306 cm\(^{-1}\) and is denoted as a FeO stretching vibration (Figure 5a). Strong Raman bands are observed at 261 and 279 cm\(^{-1}\). Intense Raman bands for wardite observed at 258 cm\(^{-1}\) are thought to be related to the O-Al-O skeletal stretching vibrations. Other Raman bands for cyrilovite are observed at 117, 131, 148, 156 and 165 cm\(^{-1}\). These bands are simply described as lattice vibrations.

The Raman spectrum of cyrilovite in the 2600 to 3800 cm\(^{-1}\) spectral range is displayed in Figure 6a. The infrared spectrum of cyrilovite in the 2600 to 3800 cm\(^{-1}\) is reported in Figure 6b. Intense Raman bands for cyrilovite are found at 3328 and 3452 cm\(^{-1}\) with a broad shoulder at 3194 cm\(^{-1}\). These bands are assigned to OH stretching vibrations. In the infrared spectrum (Figure 5b), sharp infrared bands are observed at 3485 and 3538 cm\(^{-1}\). Broad infrared bands are found at 2893, 3177 and 3311 cm\(^{-1}\). Tarte et al. [16] reported the infrared
spectrum of wardite and cyrilovite. They found that O-H stretching frequencies are distributed into 2 spectra regions: 2 very broad bands near 2950 and 3300 cm\(^{-1}\), which are due to H\(_2\)O molecules engaged in short H bonds; and 2 very sharp and strong peaks (3550 and 3495 cm\(^{-1}\) for pure cyrilovite, 3621 and 3555 cm\(^{-1}\) for pure wardite) due to the stretch of hydroxyl group. Sharp infrared bands for wardite are observed at 3544 and 3611 cm\(^{-1}\) and are attributed to the OH stretching vibrations of the hydroxyl units. A sharp band in the infrared spectrum is observed at 3480 cm\(^{-1}\) for the sample from Utah. This band may be due to FeOH stretching vibrations. Breitinger et al. [15] found infrared bands at 3520 (vw), 3545 (s), 3585 (sh) and 3613 cm\(^{-1}\) (m). Breitinger et al. states that the \(\nu\) (OH) modes in the two independent pairs of symmetry-correlated OH groups classify as 2a + 2b; with the correlation splitting between a and b species depending on the distances in each of the pairs [15]. The \(\nu\) (OH) region of IR spectra of wardite shows two sharp bands (3613 and 3545 cm\(^{-1}\)) with two weak shoulders or satellites (3580 and 3520 cm\(^{-1}\)). It is likely that the two sharp infrared bands are due to two independent and non-equivalent OH units. The two sharp shoulder bands may be attributed to the Al–OH–Fe groups. Broad infrared bands are observed at 2876 and 3268 cm\(^{-1}\) are assigned to water stretching vibrations. It is probable that some of the component bands are due to overtones and combination of the water bending and librational modes. The position of the water stretching vibration provides evidence for strong hydrogen bonding and that water is involved in different hydrogen bonding arrangements. The band at around 2893 cm\(^{-1}\) gives an indication that water is very strongly hydrogen bonded in the cyrilovite structure.

The Raman spectrum of cyrilovite in the 1400 to 1800 cm\(^{-1}\) spectral range is illustrated in Figure 7a. The spectrum suffers from a lack of signal; this is not unusual as water is a very weak Raman scatterer. Raman bands are observed at 1599 and 1634 cm\(^{-1}\). These bands are assigned to water bending modes. In contrast, the infrared spectrum of cyrilovite is displayed in Figure 7b, where significant intensity is observed. Water is a very strong infrared absorber. Infrared bands are observed at 1599 and 1650 cm\(^{-1}\) and are assigned to water bending modes. Infrared bands for wardite are observed at 1549, 1670 and 1748 cm\(^{-1}\). The bands in this region result from correlation splitting as a result of the short distance and orientation of the H\(_2\)O molecules. Additional bands for wardite are observed at 1417 and 1476 cm\(^{-1}\). The assignment of these bands is due to OH deformation modes. The presence or absence of these bands depends upon the Fe/Al ratio in the cyrilovite/wardite mineral samples.
CONCLUSIONS

Raman spectroscopy complimented with infrared spectroscopy has been used to study the molecular structure of the mineral cyrilovite. The structure of cyrilovite is unusual in that it belongs to a unique symmetry class, namely the tetragonal-trapezohedral group. The structure of wardite contains layers of corner-linked –OH bridged MO₆ octahedra stacked along the tetragonal C-axis in a four-layer sequence and linked by PO₄ groups. As a consequence at the molecular level non-equivalent phosphate units exist in the structure. As a consequence multiple phosphate vibrational modes are observed.

The mineral cyrilovite is a mineral which shows very strong fluorescence when the laser wavelength of 633 nm is used. The fluorescence is probably due to electronic bands as the result of impurities. The use of the 785 nm excitation enables the fluorescence of the wardite minerals to be overcome. The fluorescence bands are superimposed upon the Raman spectrum and appear as intense broad bands.

Acknowledgments

The financial and infra-structure support of the Queensland University of Technology, Chemistry discipline is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the instrumentation. The authors would like to acknowledge the Center of Microscopy at the Universidade Federal de Minas Gerais (http://www.microscopia.ufmg.br) for providing the equipment and technical support for experiments involving electron microscopy. R. Scholz thanks to FAPEMIG – Fundação de Amparo à Pesquisa do estado de Minas Gerais, (grant No. CRA - APQ-03998-10).
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